

ELECTROLYTES AND ITS ADDITIVES USED IN ALUMINUM REDUCTION CELL: A REVIEW

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Abstract

The electrolyte is considered to play the role of blood in an aluminum reduction cell and performs several vital functions as the charge transfer, the mass dissolution and transfer, the electrode products separation and the electrical work dissipation. The proper performance of listed functions is completely determined by the physical and chemical properties, which namely are the electrical conductivity, the viscosity, the vapor pressure, the liquidus and solidus temperatures, the density, the surface tension, the solubility and the dissolution rate of oxides, aluminum, carbon and the various connections and by operating conditions, which namely are the temperature, the current density, the anode-cathode distance, etc. The electrolyte affects the current efficiency and the cell voltage, which determines the specific energy consumption and the total cost of aluminum. This is the reason why different electrolytes and additives have been in the spotlight of the researchers and the enterprises for decades. This article presents the brief information about the influence of additives in the cell utilizing traditionally used sodium cryolite and different low-temperature electrolytes on physical-chemical properties and concentrates on the latest works which have not been included in widely known textbooks. The article also contains new experimental results obtained by the authors and devoted to the effective electrical conductivity of suspended unconventional electrolytes.

Keywords: electrolyte properties, low-temperature electrolytes, cryolite melt, suspension electrolyte, Additives.

1 Introduction

Aluminum is one of the highly smelted metals in the world as bauxite being one of the most abundant ore in the earth's crust from which alumina is extracted. Earlier, almost 70 million ton of aluminum is been smelted as it is used in different ways like in construction, fabrication of auto-parts and aircrafts and so on because of its light density and high strength at the same time [1]. Hall-Heroult's process, have been in use for the production of aluminum for over 120 years and the process is continued to be used until date. A typical Hall-Heroult Cell and the concept of alternatively designed cell with vertical electrodes proposed by the authors of the current paper, which can be used with suspension electrolytes and has the detailed description in [2] , are shown in figure 1.

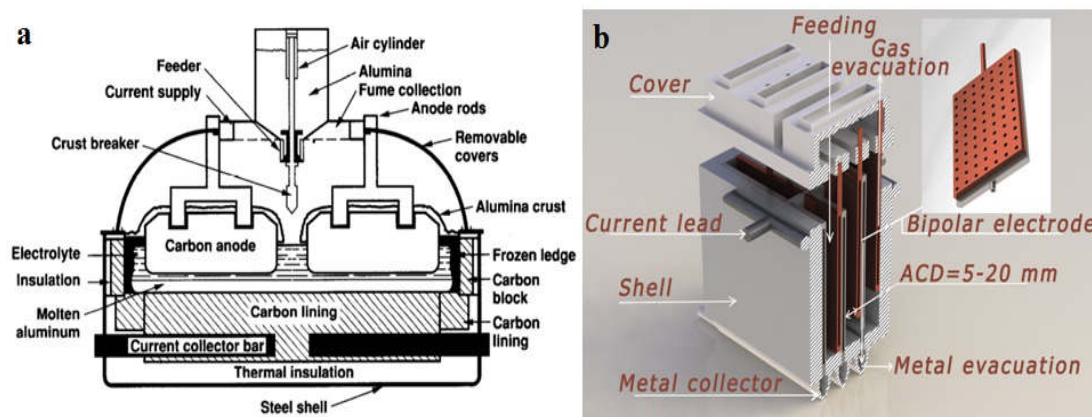
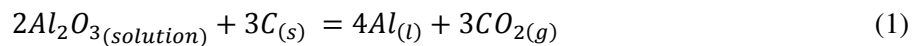


Figure 1 – Schematic diagram of a: Hall-Heroult Cell [3]; b: Novel design cell

In the Hall-Heroult **process**, carbon anode and aluminum cathode are used and the alumina fed to the cell is dissolved in the fluoride bath of molten cryolite-based electrolyte at 960 °C. The main reaction occurred in this process is



In the reaction (1), the dissolution of alumina results in the formation of oxyfluoroaluminates while using sodium cryolite, where its structure depends on the electrolyte composition. The oxyfluoroaluminates formed are AlOF_x^{1-x-} , $\text{Al}_2\text{OF}_x^{4-x-}$, $\text{Al}_2\text{O}_2\text{F}_x^{2-x-}$, Al_4OF_8 and $\text{Al}_4\text{OF}_{10}$ out of which AlOF_2^- , $\text{Al}_2\text{OF}_6^{2-}$ and $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ are the most stable and involved structures in the electrolysis process [4], [5]. Their presence in the cryolite mixture increases the electrical resistance, viscosity of the liquid and decreases the vapor pressure of the melt. The formation of the anionic fluoro-aluminates in the cryolite melt depends on the cryolite ratio (CR) and concentration of alumina dissolved. The complex ionic form such as AlF_4^- , AlF_5^{2-} , AlF_6^{3-} , $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ and $\text{Al}_2\text{OF}_6^{2-}$ are formed at $1 < \text{CR} < 3$ and $\text{Al}_3\text{O}_4\text{F}_4^{3-}$ complex ion is only formed at $3 < \text{CR} < 4$ in alumina saturated melts [6], [7], [8]. The structural properties of solid cryolite were widely studied by Kirik et al. [9] and Samoilo et al. [10].

The bath is a subsystem of an aluminum reduction cell and is being considered as the dissipative structure. It performs the following basic functions:

- Charge transfer;
- Substance dissolution and transfer;
- Cathodic and anodic products separation;
- Electrical work dissipation, maintaining the enthalpy of substance at the high temperature and providing required heat loss into the environment.

Bath composition and temperature highly **affect** its properties and consequently the technical and economic indicators of the electrolysis.

The electrolyte used presently in the smelters around the world **is based on** sodium cryolite system and its operating temperature is around 960 °C. Many other reactions occur besides reaction (1) in the cell. Alumina fed in the cell contains the impurities of Li and K, which changes the composition of the melt affecting the current efficiency and the operating conditions of the cell. As the operating temperature of the cell with electrolyte based on sodium cryolite is high, it results in a quick corrosion of the cell parts reducing the lifetime of a cell.

The inert (non-consumable or carbonless) anodes [11] [12] are highly desirable in aluminum production. Sodium cryolite in the electrolysis process eliminates the use of most of the metals which are highly (!confusing word) towards high-temperature melts. Using low-temperature electrolytes gives the scope to conduct tests on the materials which can be operated at temperatures around 750 – 800 °C [13]. Potassium cryolite ($\text{KF} - \text{AlF}_3$) can be operated between 680 – 800 °C [14], [15]. The solubility of alumina increases by 30% while using potassium cryolite than compared to sodium cryolite but the electrical conductivity of the potassium cryolite is low compared to that of sodium cryolite. Many experiments were conducted to characterize the $\text{KF} - \text{NaF} - \text{AlF}_3$ melt which can be used as low-temperature electrolyte.

In the year 1971, scientists from Alcoa patented a process by which aluminum can be extracted from AlCl_3 (replacement of alumina as a feed) by using molten alkali metal chloride or alkaline earth metal chlorides as electrolyte at 730 °C but the main problem was the unavailability of pure AlCl_3 . In 1979, it was claimed by Alcoa scientists that the $\text{AlCl}_3 - \text{LiCl}_3$ molten system can be used as a low-temperature electrolyte at 700°C as discussed in the patents [16]-[19]. Currently, several researchers are studying the behavior of the suspension electrolyte with the operational temperature between 700 and 800 °C. The suspension particles (being alumina) can be added up to 30 vol.% fraction in the melt, which drastically reduces the electrical conductivity, and to compromise this issue, the anode-cathode distance have to be reduced. The main purpose of alumina suspension particles in the melt is to reduce the corrosion, which damages the cell parts, the anodes, and to slow down the mass transfer of corrosion products into aluminum. By using suspension electrolytes, the use of inert anodes can be encouraged. Minh et al. [20] discussed the chemical fundamentals and the properties such as electrical conductivity, operation temperature, vapor pressure, corrosiveness, current efficiency, diffusivity, viscosity and electrode kinetics of molten salt electrolytes.

The bath composition is generally optimized to minimize specific energy consumption which can be expressed by the equation:

$$W = f_1 \left(\frac{E_p + f_2(i\rho l)}{\eta} \right) \quad (2)$$

where, W is the Specific energy consumption, E_p is the EMF, i is the current density, ρ is the specific resistance, l is the inter-electrode distance and η is the current efficiency.

By minimizing the specific resistance of the electrolyte, the specific energy consumption of the cell can be reduced.

2 Electrolytes and influence on its properties by the additives

2.1 NaF-AlF₃ electrolyte and its additives

In the Hall-Heroult process, the bath is based on sodium cryolite with operating temperature 955 – 970°C which is said to be the traditional industrial electrolyte. There are many factors that influence the performance of the cell. Inclusion of additive in the electrolyte changes the electrical conductivity of the system drastically [21]. It is well known that the industries desire to use electrolytes with more acidic content (Cryolite ratio (CR) between 2.12 and 2.30). An increase in AlF₃ content in the molten cryolite increases the acidic nature of the electrolyte. Decrease in CR (NaF mol% / AlF₃ mol%) decreases the solubility of alumina in the melt [22]. Maintenance of the frozen side ledge becomes extremely difficult at low CR's.

J. Wang et al. [23] discussed the behavior of the sodium cryolite melt with high Li⁺ and K⁺ ions concentration. The presence of the Li⁺ and K⁺ ions in the electrolyte is due to the use of impure alumina with high content of Li₂O and K₂O. The electrolyte with high content of LiF and KF provides slightly less current efficiency compared to the pure sodium cryolite melt. However the electrical conductivity of the electrolyte containing Li⁺ is higher than that of the regular electrolyte which can favor energy saving. Influence of CaF₂ addition on the electrical conductivity of the sodium cryolite was tested in [24]. It was observed that with the increase in the CaF₂ concentration, the electrical conductivity decreases as shown in figure 2.

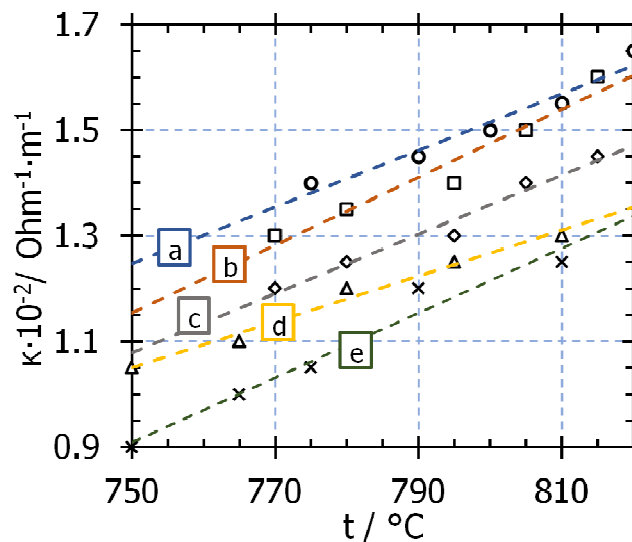


Figure 2 – Electrical conductivity of the (NaF – AlF₃) – CaF₂ mixture with (CR = 1.5) depending on the CaF₂ (mol. %) concentration: a-2.3, b-4.6, c-7.8, d-9.4, e-11 [24]

Dewing et al. [25] conducted tests to find the influence of additives in the electrolyte on the current efficiency of the cell. Inclusion of LiF leads to an increase in the current efficiency. It was also observed that the addition of CaF₂ in electrolyte does not have direct effect on the current efficiency of

the cell but it affects the superheat which influences the current efficiency. An equation (3) was obtained to determine the current efficiency influenced by the additives and is stated below.

$$\lg(\Delta\eta_i) = 0.0095 \cdot \Delta T - 0.019 \cdot C_{\text{AlF}_3} - 0.060 \cdot C_{\text{LiF}} + C \quad (3)$$

where $\Delta\eta_i$ is the current efficiency loss, ΔT is the superheat, C_{AlF_3} – wt.% of AlF_3 , C_{LiF} – wt.% LiF , C – numerical constant related to the cell functioning

Korenko et al. [26] [27] investigated the impact of SiO_2 content on the electrical conductivity and viscosity of the cryolite mixture ($\text{NaF} - \text{AlF}_3$ of eutectic composition) in tube–cell (fabricated with pyrolytic boron nitride) with stationary electrodes. In range of 0 to 10 mole % of SiO_2 , the conductivity increased and in a range of 10 to 40 mole % the drop in the electrical conductivity was observed. Equation (4) shows the relationship between the electrical conductivity and the SiO_2 content.

$$\kappa = 1.127 - 0.01750 \cdot C_{\text{SiO}_2} + 0.001789 \cdot T \quad (4)$$

where κ is the electrical conductivity in S/cm, T is the temperature (950-1120) in °C and C_{SiO_2} is the mole fraction of SiO_2 .

The viscosity of $\text{NaF-AlF}_3\text{-SiO}_2$ mixture decreases while the content of SiO_2 is raised from 0 to 10 mole % and starts to increase when the SiO_2 proportion is from 10 to 40 mole %. Equation (5) is formulated by using regression modelling to demonstrate the relation between viscosity, SiO_2 content and temperature.

$$\mu = 19.85 - 0.01737 \cdot T + 0.07618 \cdot C_{\text{SiO}_2} \quad (5)$$

where μ is the viscosity of the melt in mPa·s, T is the temperature (1010-1120) in °C and C_{SiO_2} is the mole fraction of SiO_2 .

The viscosity of the melt increases with high proportions of SiO_2 because of the formation of complex ions like SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$ and $\text{Si}_3\text{O}_{10}^{8-}$ as they lead to the growth of the bigger network structure [28]. The inclusion of basic oxides in the melts destroys the network structure of complex ions resulting the reduction of viscosity of the melts. The relation between the electrical conductivity and viscosity was discussed by Zhang et al. [29], where the electrical conductivity increases **as the viscosity decreases**.

Solubility of aluminum in sodium cryolite melt was determined by Vasyunina et al. [27]. The samples of the melt were frequently tested by rapid cooling the electrolyte samples and the content of metal present in the melt was determined by using the gas volumetric analysis. The influence of additives such as lithium fluoride, aluminum fluoride and potassium fluoride on the solubility of aluminum in the melt was also determined. Few conclusions were made:

1. Decrease in the CR ($\text{NaF mol\%/AlF}_3 \text{ mol\%}$) from 2.5 to 2.2 at a constant overheating with the saturation of the electrolyte with alumina reduces the solubility of the metal from 0.042 to 0.023 wt.%.

2. Further decrease of the CR, less than 2.1 does not show any influence on the solubility of the metal in the melt.

3. Addition of 5 wt.% of KF considerably reduces the solubility of the aluminum in the melt.

4. An introduction of 3 wt.% of LiF reduces the aluminum solubility.

5. The increase in CaF_2 from 4 to 6 wt.% increases the solubility of the metal in the melt.

Dissolution rate of alumina in $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$ was studied by reducing the CR value less than 2.1 to make the melt acidic by increasing the AlF_3 content in order to achieve high current efficiencies [31]. Reducing the CR value decreases the solubility of aluminum in the melt increasing the current efficiency and dropping the liquidus temperature of the electrolyte giving the scope to use inert anodes. It was noted that by reducing CR below 2.1 up to 1.5, there is a drastic drop in the solubility and dissolution rate of alumina in the melt. The authors also mentioned that a cell with 300 kA load could only achieve proper electrolysis operation when the CR is greater than 1.8, as low CR values minimize the dissolution rate of alumina.

The density of sodium cryolite when AlPO_4 is added was investigated in [32]. Sodium cryolite melts with different CR (1.5-3.0) were tested to determine their density. It was determined that for the sodium cryolite with AlPO_4 additive, the density of the system decreases with decrease in the CR of the

melt. The density of the system linearly decreases as the AlPO_4 content increases as shown in equation (6). The density of the melt almost remains the same at CR 3.0 irrespective of the increase in the AlPO_4 content.

$$\rho = 1.7217 - 0.00142 \cdot C_{\text{AlPO}_4} + 0.1490 \cdot CR \quad (6)$$

where ρ is the density of the $(\text{NaF} - \text{AlF}_3) - \text{AlPO}_4$ melt in g/cm^3 , C_{AlPO_4} is the wt.% AlPO_4 ,

Kubinakova et al. [33] determined the effect of additives in composite form of Al_2O_3 - CaF_2 , Al_2O_3 - MgF_2 and Al_2O_3 - CaF_2 - LiF in low-temperature sodium cryolite. Studies found that an increase in the concentration of AlF_3 up to 45 mol% decreases the melting temperature of the electrolyte to 700 °C as well as decreases the electrical conductivity. Findings show that the Al_2O_3 , CaF_2 and MgF_2 causes the decline in the electrical conductivity of the multi-structural electrolyte except LiF , which improves the electrical conductivity. The reason behind the decrease in the electrical conductivity with the addition of CaF_2 and MgF_2 is that the Ca^{2+} and Mg^{2+} cations have high charge densities forming anionic complexes obstructing the path of charge carriers [34],[35]. Kubinakova et al. [33] formulated an equation (7) to show the dependence of the compositions on the electrical conductivity of the system. The research conducted in the past by Hives et al. [36] and Fellner et al. [37] reflected the same results. Increase in the composition of CaF_2 and MgF_2 in the melt lowers the conductivity (κ).

$$\kappa = 3.521 - 3.749 \cdot C_{\text{AlF}_3} + C_{\text{Al}_2\text{O}_3} \cdot (18.959 - 75.984 \cdot C_{\text{AlF}_3}) - 0.828 \cdot C_{\text{CaF}_3} + C_{\text{MgF}_2} \cdot (4.00 - 13.585 C_{\text{AlF}_3}) + C_{\text{LiF}} \cdot (-4.773 + 10.806 \cdot C_{\text{AlF}_3}) \quad (7)$$

where C_{AlF_3} is the wt.% of AlF_3 , $C_{\text{Al}_2\text{O}_3}$ is the wt.% of Al_2O_3 , C_{CaF_3} is the wt.% of CaF_3 , C_{MgF_2} is the wt.% of MgF_2 and C_{LiF} is the wt.% of LiF .

Bao et al. [38] investigated the influence of ZrO_2 on the electrical conductivity when added to NaF - AlF_3 - CaF_2 - Al_2O_3 - ZrO_2 melt. The tests were carried out in a tube type cell with a fixed cell constant. A study was carried out for five different CR's by varying the wt.% of ZrO_2 from 0 to 5. An increase in 1 wt.% of ZrO_2 reduces the electrical conductivity of the melt by 0.02 S/cm with a temperature range of 950-1010 °C. Increase in the CR(NaF mol% / AlF_3 mol%) improves the electrical conductivity as the decrease in the concentration of AlF_3 reduces the number of complex ions and enhancing the number of mobility ions. The regression equation (8) is formulated based on the data acquired by Bao et al. [38].

$$\kappa = 0.004933 \cdot T - 0.03101 \cdot C_{\text{ZrO}_2} + 0.6616 \cdot CR - 4.112 \quad (8)$$

where C_{ZrO_2} is the wt.% of ZrO_2 , CR ranging from 2.2 to 2.5, temperature ranging from 950 to 1010 °C

Frazer et al. [39] determined the alumina solubility and the diffusion rate of dissolved alumina in NaF - AlF_3 eutectic melt. The solubility is said to be 3.2 ± 0.3 wt % in NaF - AlF_3 eutectic at 750 °C. When CaF_2 (5 wt %) is added to the NaF - AlF_3 eutectic, alumina solubility becomes equal 3.0 ± 0.3 wt % at 750 °C. It implies that the addition of CaF_2 has the negative impact on the alumina solubility in the melt. The diffusion rate of dissolved alumina was $2.2 \times 10^6 \text{ cm}^2 \cdot \text{s}^{-1}$ in NaF - AlF_3 eutectic melt at 750 °C, which is five times less than the value achieved through the traditional bath operated at 960°C (a low diffusion rate leads to a slow mass transfer).

The surface tension of the NaF - AlF_3 system (NaF 55 mole % and AlF_3 45 mole %) with the temperature dependency was determined by Silny et al. [40]. The surface tension was obtained by knowing the maximum pressure exhibited by bubble formed on the tip of a capillary. The capillary is immersed in the molten cryolite to a known depth and at a given temperature. The maximum bubble pressure is reached when the bubble forms a hemisphere with a radius equalizing the radius of the capillary. The surface tension is calculated by using the following equation (9) from [41],

$$\sigma = \frac{r}{2} (P_{\text{max}} - g\rho h) \quad (9)$$

where r is the capillary radius, P_{max} is the maximum bubble pressure, g is the gravitational constant, ρ is the density of the melt and h is the depth of immersion of the capillary.

The surface tension in the system decreases linearly with the temperature (740 to 815°C) as shown in equation (10): .

$$\sigma = 2.6033 - 9.2738 \cdot 10^{-4} \cdot T \quad (10)$$

where σ is the surface tension ($^3\text{N/m}$) and T is the temperature in the range (740-815) °C

The influence of Al_2O_3 on the local-structure and transport properties of $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$ was investigated by Lv et al. [42]. The studies reveal that the AlF_4^- , AlF_5^{2-} and AlF_6^{3-} complex ions exist simultaneously in $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$ molten system. At low Al_2O_3 concentrations (approximately 1-2 wt. %) in the melt, the most dominant complex ion is AlF_6^{3-} . The AlF_4^- , AlF_5^{2-} and AlF_6^{3-} complex ions have equal proportions in the molten salt when Al_2O_3 concentration is 3 wt % and the AlF_4^- ion tends to be dominant among others when the Al_2O_3 concentration is 4 wt %. Increase in the concentration of Al_2O_3 reduces the ionic conductivity of the molten salt and simultaneously raises the viscosity. It is due to the formation of complex structure in the molten salt as the Al_2O_3 acts as a bridge connecting the ionic structure networks, which increases the polymerization degree of local structure in the molten salt.

As earlier discussed, the formation of the fluoro-aluminates in the molten cryolite system depends on the CR as follows [6], [7], [8]:

1. The complex ions AlF_4^- , AlF_5^{2-} , AlF_6^{3-} , $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ and $\text{Al}_2\text{OF}_6^{2-}$ are formed at $1 < \text{CR} < 3$
2. The $\text{Al}_3\text{O}_4\text{F}_4^{3-}$ complex ion is only formed at $3 < \text{CR} < 4$ in alumina saturated melts.

2.2 KF-AlF₃ electrolyte and additives

The low temperature melts were desirable for the electrolysis since long time as they reduce the corrosion rate of the cell parts and increase the cell lifetime. Pure potassium cryolite dissolves more alumina than sodium cryolite. But the electrical conductivity of the potassium cryolite is rather low and decreases with decrease of the temperature (680-820°C) and increases with the increase in CR (mole fraction of KF divided by mole fraction of AlF_3) between 2.2 and 3.0. The equation (11) was formulated by using the regression modeling from the data acquired by Kryukovsky et al. [43].

$$\kappa = 0.0026 \cdot T - 0.8788 \quad (11)$$

Xu et al. [44] calculated the thermodynamic properties of KF-AlF_3 and determined that the complex ions formed are AlF_6^{3-} , AlF_5^{2-} and AlF_4^- similar to that of the NaF-AlF_3 and LiF-AlF_3 systems. The AlF_6^{3-} complex ion is tend to be more stable in the KF-AlF_3 system than in the NaF-AlF_3 or LiF-AlF_3 melts due to the weakest action of cation K^+ on the ligand F^- . It makes the electrical conductivity of KF-AlF_3 lower than that of the NaF-AlF_3 system where AlF_6^{3-} is dissociated into AlF_5^{2-} , AlF_4^- and AlF_3 in steps resulting in the easy charge carriers transportation. The same was stated by Tsirlina et al. [45] and Nazmutdinov et al. [46].

The electrical conductivity of KF - NaF - AlF_3 melts were investigated by Yang et al. [47]. The addition of KF in the sodium cryolite results in the decrease in the melting temperature. The continuously varying cell constant technique was used to measure the electrical conductivity of KF - NaF - AlF_3 melt with varying parameters like NaF content, alumina content and CR at different temperatures. The effect of the NaF content on the conductivity of KF - NaF - AlF_3 melt was examined. The cryolite ratio of this particular melt is the sum of mole fraction of NaF and KF divided by the mole fraction of AlF_3 . At CR = 1.3 the conductivity of the melt was measured with following contents:

1. KF 57.4 mol%;
2. NaF 15 mol%, KF 42.7 mol%;
3. NaF 30 mol%, KF 27.4 mol%;
4. NaF 45 mol%, KF 12.4 mol% and
5. NaF 57.4 mol%

The temperatures were in the range from 750-820°C with 10°C interval. The dependence can be expressed by the equation (12).

$$\kappa = 0.002776 \cdot T + 0.001393 \cdot C_{\text{NaF}} - 0.0192 \quad (12)$$

where C_{NaF} is the mole % of NaF in the NaF - KF - AlF_3 system.

This is due to the fact that the radius of Na^+ ($1.02 \times 10^{-10}\text{m}$) is smaller than K^+ ($1.38 \times 10^{-10}\text{m}$) and hence, the Na^+ ion migration speed is tend to be higher than that of K^+ , which

is the reason why the electrical conductivity of the melts increases with the increase of NaF content. Similarly, the electrical conductivity was calculated by varying the alumina content and changing CR for different temperatures between 750 - 820°C with 10°C interval and the findings show that with an increase in the alumina content, the electrical conductivity decreases and with an increase in CR, the conductivity increases.

Apisarov et al. [48] measured the electrical conductivity of the KF – AlF₃ system containing LiF and alumina. It was determined that by increasing LiF content, the electrical conductivity of the molten electrolyte increases and by increasing alumina content, the electrical conductivity slightly drops. Equation (13) shows the relation between the conductivity, the temperature and the content of alumina in the electrolyte composition at CR=1.3 (KF mol% /AlF₃ mol%)

$$\kappa = 0.1336 + 0.001547 \cdot T - 2.25 \cdot C_{Al_2O_3} \quad (13)$$

where, $C_{Al_2O_3}$ is the wt.% Al₂O₃ in KF – AlF₃ – Al₂O₃ (CR= 1.3) electrolyte. $T=680-800^\circ\text{C}$.

For all compositions (w.r. to LiF content) the electrical conductivity of the melt increases with a temperature raise. The equation (14) was derived as below:

$$\kappa = 0.0351 + 0.001692 \cdot T + 1.375 \cdot C_{LiF} \quad (14)$$

where, C_{LiF} is the wt.% LiF in KF – AlF₃ – LiF (CR= 1.3) melt. $T = 680-800^\circ\text{C}$

The liquidus temperature and the density of the KF – AlF₃ system with the addition of AlPO₄ to the melt was determined by Vaskova et al. [49]. The liquidus temperature and the density of the system was determined for $1.5 \leq CR \leq 3$ and at different AlPO₄ contents. The liquidus temperature of the system tends to decrease with the increase in the AlPO₄ content and as the CR is reduced, the liquidus temperature of (KF – AlF₃) – AlPO₄ system falls (figure 3).

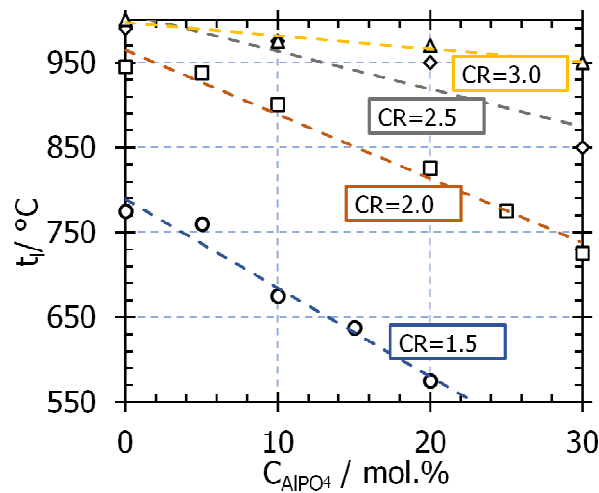


Figure 3 – Liquidus temperatures of (KF – AlF₃) – AlPO₄ system at different cryolite ratios with increasing AlPO₄ content [49]

The density of the system also decreased with an increase in the AlPO₄ content and increases with an increase in CR. The density of the system almost remains the same at $CR \geq 3.0$ irrespective of the increase in the AlPO₄ content similar to the NaF – AlF₃ – AlPO₄ system that can be seen in figure 4.

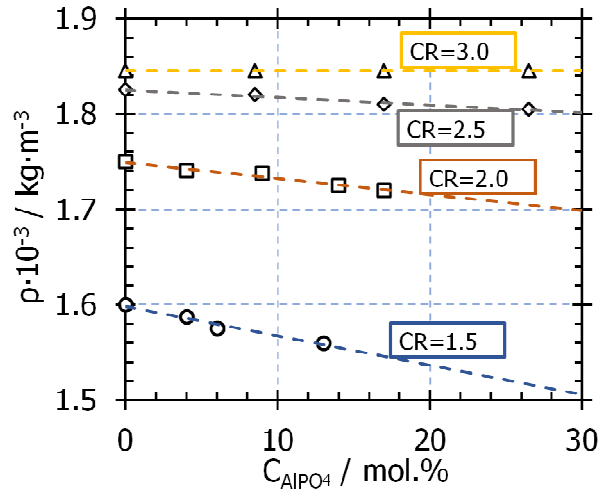


Figure 4 – Density of (NaF – AlF₃) – AlPO₄ system, at 1050 °C, at various CR [49]

2.3 Chloride melts

Even though fluoride melts are used for aluminum electrolysis, the desire to use low temperature electrolytes have made researchers to do extensive research towards chloride melts. Mostly, the Chloride melt would be the combination of AlCl₃ and alkali metal halides like NaCl, LiCl, KCl, BeCl₂, CaCl₂, MgCl₂, BaCl₂. Usually NaCl is highly preferred, as AlCl₃ – NaCl combination has low melting temperature. AlCl₃, Al₂S₃ and other materials [50] have considerably high solubility in chlorides. The electrical conductivity of various chloride melts at different operating conditions and molar fractions were discussed by Redkin et al. [50]

Minh et al. [51] investigated the electrolysis of Al₂S₃ at 750°C by using AlCl₃ – MgCl₂ – NaCl – KCl electrolyte, as Al₂S₃ dissolve in the electrolyte and electrolysis produces aluminium and sulphur. The anodic current density plays a crucial role in this process and it varies in the range 0.2 – 1.2 A/cm² with current efficiencies of 75 – 85% (the efficiency increases with the increase of the current density). Dependence between solubility of Al₂S₃ ($C_{Al_2S_3}^s$) and the composition of electrolyte is shown in figure 5.

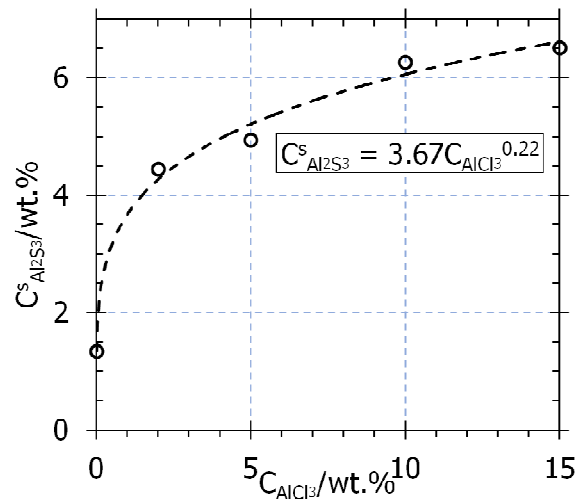


Figure 5 – Solubility of Al₂S₃ vs. AlCl₃ content (C_{AlCl_3}) in the melt [50]

The cathode has a limiting current density of 0.3 A/cm² resulting in the low productivity. It was observed that the solubility of Al₂S₃ strictly depends on the amount of AlCl₃ added in the electrolyte where the solubility of aluminum sulphur increases with the increase in the content of AlCl₃ in the melt and can be seen in Figure 5.

The reduction of aluminum was performed in the $\text{CaCl}_2 - \text{NaCl} - \text{Al}_2\text{O}_3$ molten electrolyte with 71~87 wt.% of CaCl_2 (the rest being NaCl) by Xie et al. [52]. The temperature was varied between 550-800°C. Electrical conductivity was measured. From acquired results an equation (15) was formulated.

$$\kappa = -1.300 + 0.0044 \cdot T - 0.04 \cdot C_{\text{Al}_2\text{O}_3} \quad (15)$$

where $C_{\text{Al}_2\text{O}_3}$ is the wt.% Al_2O_3 in the $\text{CaCl}_2 - \text{NaCl} - \text{Al}_2\text{O}_3$ system, $T = 550-750^\circ\text{C}$

With an increase in the CaCl_2 content, the electrical conductivity and the density of the electrolyte decreases. Equation (16) illustrates the effect of the increased CaCl_2 content on the electrical conductivity of the electrolyte. Conclusion is made by saying that the CaCl_2 -based electrolyte can actually be used and its lower melting temperature seems to be an attractive property.

$$\kappa = 0.221 + 0.003664 \cdot T - 1.584 \cdot C_{\text{CaCl}_2} \quad (16)$$

where C_{CaCl_2} is the wt.% CaCl_2 in $\text{CaCl}_2 - \text{NaCl} - \text{Al}_2\text{O}_3$ melt, $T = 600-800^\circ\text{C}$

Balaraju et al. [53] investigated the solubility of alumina in the $\text{NaF-KCl-Al}_2\text{O}_3$ mixture. The studies showed that with increase in the NaF content in the mixture, the alumina solubility tends to increase. That can be clearly seen in Table 1.

Table 1. Solubility of Alumina (Mass Percent, 100 w) in Molten NaF-KCl Mixtures

Composition of KCl-NaF (mole %)	Alumina solubility (100 w)
80-20	0.5 (740 °C)
70-30	0.9 (760 °C)
50-50	1.1 (740 °C)
30-70	1.2 (650 °C)
20-80	1.2 (670 °C)

2.4 Suspension electrolyte

The concept of suspension electrolyte was developed by T.R. Beck. The main idea of using suspension electrolyte is to maintain it saturated with alumina, to reduce the solubility of oxides, to minimize the corrosion rate of non-carbon anodes and to increase the cell lifetime. In [54] a eutectic $\text{NaF} - \text{AlF}_3$ melt with and without addition of $\text{KF} - \text{AlF}_3$ and $\text{LiF} - \text{AlF}_3$ was examined in 1-40 A laboratory cell at around 750°C. Copper anode and TiB_2 cathode were used and the alumina particles were fed in suspension at anode-electrolyte interface to avoid anode effect. The oxygen evolved at the anode keeps the alumina particles suspended, so it is important to have a continuous removal of the aluminum from the cell having an auxiliary anode to avoid the stoppage of oxygen evolution from the anode.

The cell would have a thermodynamic potential of 2.35V. The anodic overvoltage of 0.3 V was measured at 0.5 A/cm² current density and the cathodic overvoltage was negligible. The bath's ohmic drop for anode cathode distance of 1.3 cm was said to be 0.65 V. The effective bath conductivity was said to be 1.0 S/cm. The current efficiency of the cell was reported to be 50% and it depends on the surface area of the aluminum (A) near the anode to current supplied (I). The current efficiency increases with the decrease in (A/I) ratio and this can be achieved by consistent removal of aluminum near the anode and if this is implemented accurately, nearly 100% current efficiency can be achieved.

Theodore R. Beck proposed commercial cell design, which uses alumina slurry in the electrolyte, with the conditions mentioned in his patents [55]-[57]:

- A eutectic $\text{NaF} - \text{AlF}_3$ electrolyte with freezing point of 695 °C with the combination of $\text{KF} - \text{AlF}_3$ and $\text{LiF} - \text{AlF}_3$ eutectics having melting temperature of 750°C.
- Alumina slurry content of 5 – 10 wt.% with particle size of less than 10 µm is added to the electrolyte.
- Vertical copper mono-polar anode and Titanium boride cathode with the minimum anode cathode distance at around 1.3 cm.
- Continuous removal of aluminum to maintain better current efficiency.
- The horizontal auxiliary oxygen evolving anode which avoids settling down of alumina particles at the bottom.

Yasinskiy et al. [58], [59] investigated the sedimentation behavior of alumina suspension based on low-temperature electrolyte system $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$. The value of maximum packing fraction for smelter grade alumina was estimated to be approximately as high as 0.32 at which the particles have extremely low or zero sedimentation velocity. The main factors determining this value were named to be poly-dispersity (which was calculated to be 0.42), the high porosity and the structural barrier which eliminates sedimentation of the particles.

3 Relative electrical conductivity of suspension electrolyte

The relative conductivity κ/κ_L (where κ – is the effective electrical conductivity of suspension, κ_L – is the electrical conductivity of pure liquid phase) plays an important role when suspended electrolyte is used as it determines the voltage drop and the specific energy consumption of the cell. Maxwell's model [62] for the prediction of κ/κ_L with the presence of suspension particles volume fraction ϕ when they act as insulators is given by:

$$\frac{\kappa}{\kappa_L} = 1 - \frac{3}{2}\phi \quad (17)$$

It is shown in [63], [64] that Bruggeman's model predicts the κ/κ_L better, when particles are multi-sized and randomly distributed:

$$\frac{\kappa}{\kappa_L} = (1 - \phi)^{3/2} \quad (18)$$

The ratio κ/κ_L of a two-phase system (suspension or foam) is considered to not depend on the nature of phases, but only on the volume fraction, shape and size of dispersed non-conductive phase ϕ .

3.1 Experiment

The experiment was carried out to find κ/κ_L of the suspension electrolyte as a function of the alumina volume fraction (ϕ). Similarity criteria [60], [61] is used to design the water model cell and electrolyte composition (20% water solution of $\text{H}_2\text{SO}_4 + 0.28\text{M CuSO}_4$) with a base being distilled water. Smelter grade alumina was provided by RUSAL (Krasnoyarsk, Russia) with 98.7% purity and $\sim 100 \text{ m}^2/\text{g}$ specific surface area.

The ratio κ/κ_L was determined from the equation

$$\kappa = \frac{l \cdot I}{\Delta U_{Ohm} \cdot S} \quad (19)$$

where $l/S=K$ – is the vessels constant, I – current, ΔU_{Ohm} – Ohmic voltage drop, determined by i -interrupt technique with potentiostat Autolab PGSTAT302n.

As K and I were constant in parallel experiments, κ/κ_L is proportional to $\Delta U_{Ohm}^L / \Delta U_{Ohm}$, where ΔU_{Ohm}^L – is the Ohmic voltage drop of pure liquid electrolyte.

To evaluate the additional effect of bubbles generated at the anode and copper deposited at the cathode due the electrolysis, the experiments were conducted at five different current densities i_a : 0.14, 0.18, 0.22, 0.25 A/cm^2 at 50°C . Nova 2.1.2 software was used to set I .

3.2 Results and discussion

The κ/κ_L ratios were determined, compared with Maxwell's and Bruggeman's models and presented in figure 6.

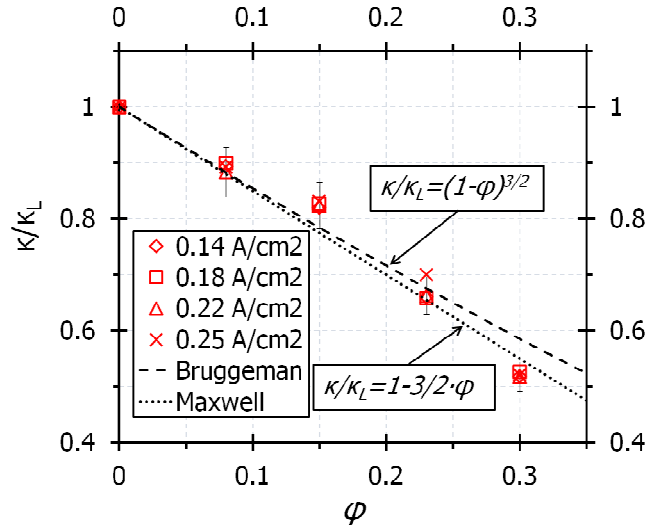


Figure 6 – Relative electrical conductivity (κ/κ_L) at different current densities i_a vs. alumina volume fraction (ϕ)

An increase in ϕ tends to decrease κ and κ/κ_L , which is in a good agreement with Cruz et al. [65] for high ionic strength liquids. The κ/κ_L ratio determined experimentally at high ϕ is lower than predicted values from the Bruggeman's model. The reason might be the influence of bubbles trapped in the suspension on the true volume fraction of non-conductive phase. The values at $\phi=0.15$ are higher than predicted ones, which is probably due to experimental error. The deviation from the models increases with ϕ , which can be explained by the fact that the effective viscosity increases, and ϕ is getting closer to maximum packing fracture estimated in [58] to be ~ 0.32 . It leads to the increase of the bubble volume fraction. The accuracy of experimental data has been estimated and mentioned in the graph in the form of error bars showing the standard deviation.

In the studied range of i_a gas generation rate (which is controlled by i_a) does not affect relative conductivity which is evidence for low experimental error introduced by the presence of gas and copper flow. Nevertheless the presented results do not have high accuracy (minor experimental error), it can be stated that the described models still can be used to characterize suspension systems in industrial processes when the precious measurements cannot be achieved.

4 Conclusion

In the article, properties of sodium cryolite, potassium cryolite, chloride based melt and suspension electrolyte are discussed. Sodium cryolite basically has high melting temperature. The melting temperature can be reduced by adding additives like calcium fluoride but it has negative effect on the electrical conductivity of the electrolyte. Potassium cryolite is a good option as it can be operated at low-temperatures. It has a poor electrical conductivity and good solubility of alumina, the vapor pressure of the system is lower than that of $\text{NaF} - \text{AlF}_3$ system because of the strong complex ions formed as latter tends to have highly diffusive ions. An addition of lithium fluoride to potassium cryolite can improve the electrical conductivity. Chloride melts can be operated at low-temperatures and aluminum chloride electrolysis can be performed by using chloride melts but high purity of AlCl_3 feed is required. Suspension electrolyte and cell design proposed by Beck seems promising. By adopting Beck's cell design, the cell geometry can be reduced, inert anode can be used. Inert anodes are desired to be used for its longer lifetime; electrolytes with low melting temperature are needed to avoid the anode corrosion of the anode. Table 2 gives the overview of the entire paper. An increase in the alumina volume fraction in the suspension electrolytic system tends to decrease the relative electrical conductivity. The electrolyte should maintain an acceptable current density and moderate alumina solubility at the low working temperature. Further research still has to be done in all the cases to obtain suitable conditions both to find a suitable electrolyte for electrolysis and novel processes [2].

Table 2. Effect of additives on the properties of the electrolyte

Electrolyte	Additives	Effects of the additives
NaF- AlF ₃	CaF ₂	Decreases electrical conductivity, decreases melting temperature [24], increases viscosity [66]
NaF- AlF ₃	LiF	Increases current efficiency, increases electrical conductivity [25]
NaF- AlF ₃	AlPO ₄	Decreases density [32]
NaF- AlF ₃	NaVO ₃	Increases density [32]
NaF- AlF ₃	Al ₂ O ₃ -MgF ₂	Decreases electrical conductivity [33]
NaF- AlF ₃	SiO ₂	Increases electrical conductivity, decreases viscosity (when C _{SiO₂} = 0 – 10 mol.%), decreases electrical conductivity, increases viscosity (when C _{SiO₂} = 11 – 40 mol.%) [26], [27]
NaF- AlF ₃	ZrO ₂	Decreases electrical conductivity [38]
KF-NaF-AlF ₃	KF	Decreases melting point, decreases electrical conductivity [47]
KF-NaF-AlF ₃	B ₂ O ₃	Increases liquidus temperature [67]
KF- AlF ₃	LiF	Increases current efficiency and electrical conductivity [48]
KF- AlF ₃	Al ₂ O ₃	Decreases electrical conductivity [49]
KF- AlF ₃	AlPO ₄	Decreases density and liquidus temperature [50]
AlCl ₃ -MgCl ₂ -NaCl-KCl	AlCl ₃	Increases solubility of Al ₂ S ₃ [51]
CaCl ₂ -NaCl-Al ₂ O ₃	CaCl ₂	Decreases electrical conductivity and increases the density [52]
CaCl ₂ -NaCl-Al ₂ O ₃	NaCl	Increases electrical conductivity [52]

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